

PATENT SPECIFICATION

NO DRAWINGS

1.033.9 12

1.033.9 12



Date of Application and filing Complete Specification July 12, 1963.

No. 27815/63.

Application made in Germany (No. F37297 IVd/39c) on July 12, 1962.

Complete Specification Published June 22, 1966.

© Crown Copyright 1966.

The inventors of this invention in the sense of being the actual devisers thereof within the meaning of Section 16 of the Patents Act 1949 are Rudolf Schroter, Leverkusen, Saarlantemer Strasse 16 Germany. Otto Bayer, Leverkusen - Bayerwerk, Carl-Rumpff - Strasse 79, Germany. Friedrich Moller, Leverkusen Adolf-Baeyer-Strasse 18 Germany. All German Citizens.

Index at acceptance: —C3 R(27K2E, 27K8E, 27K9E); C3 B(1D2C, 1N1X)

Int. Cl.: —C 08 g 23/00

COMPLETE SPECIFICATION

Process for the Preparation of Polypropylene Ether Amines

We, FARBENFABRIKEN BAYER AKTIEN-GESELLSCHAFT, of Leverkusen-Bayerwerk, Germany, a body corporate organised under the Laws of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the preparation of polypropylene ether amines.

It is known that alcohols with primary or secondary hydroxyl groups may be converted with ammonia or amines into amines in the presence of a hydrogenation catalyst ("Methoden der organischen Chemie Houben-Weyl, 1957, 4th Edition, Volume 11/1, pages 126 to 134"). Triethylene glycol has also been treated with ammonia and amines in this manner, but it has been found in this case that the reaction is not so complete and only a part of the hydroxyl groups are converted into amino groups. With polyethylene glycol the replacement of OH groups by NH₂ groups using ammonia takes place very slowly and with a very unsatisfactory yield.

It has now been found that polypropylene glycols comprising at least two hydroxy groups of many different structural formulae and molecular weights between 1000 and 4000 may be reacted with ammonia or a primary amine in the presence of a hydrogenation catalyst in the liquid phase at temperatures between 150° and 250°C to obtain high yields of polypropylene ether amines with primary or secondary amino groups.

When one considers that in the reaction of triethylene glycol with ammonia only 18% of the starting material has reacted after 31 hours,

it was not to be expected that the above process could be carried out in a simple manner both on a small scale and on a large technical scale to produce high yields and products of good quality. Moreover, the polypropylene glycols contain mainly secondary hydroxyl groups which are known to react more slowly than primary aliphatic hydroxyl groups, so that the reaction of polyhydroxyl compounds with amines may be carried out in such a way that reaction is confined virtually exclusively to the primary hydroxyl groups. Furthermore, it is natural to assume that the presence of frequent highly reactive ether groups would lead to side reactions such as splitting up of molecules and aminolysis.

Suitable polypropylene glycols for use in the process according to the invention may be obtained in a large number of ways and may contain, in addition to oxygen atoms, other atoms or groups of atoms which link alkylene groups together, such as nitrogen atoms, silicone groups, urethane groups or urea groups. The process is particularly suitable for polypropylene glycols with a molecular weight of about 1000 to 4000. These include both the polymerisation products of propylene oxide itself and the products of addition of the latter to compounds with two or more reactive hydrogen atoms such as water, glycols, triols, primary and secondary aliphatic and aromatic diamines, tertiary aliphatic and aromatic di-hydroxyalkylamines, dihydroxyalkyl-carbonamides, silicones with terminal hydroxyl groups, triethanolamine, hydrazine, ammonia, trimethylolalkanes and sugars such as sorbitol. The polypropylene glycols may be asymmetrical in the sense that

only one hydroxyl or amino group of the starting material for the formation of the addition product is etherified with a polypropylene radical. Polypropylene glycols with-
5 in the meaning of the present invention include also those compounds which contain ethylene glycol- or butylene glycol radicals in addition to the polypropylene glycol radicals. The polypropylene glycols contain mainly second-
10 ary hydroxyl groups, although a number of primary hydroxyl groups may be present.

Suitable amines for the reaction according to the invention include, for example, aniline, cyclohexylamine, propylamine, butylamine or
15 toluidine; ammonia may also be used.

General directions for carrying out the reaction may be found, for example, in "Methoden der organischen Chemie, Houben-Weyl, 1957, 4th Edition, Volume 11/1, pages
20 126 to 134". Suitable hydrogenation catalysts are, for example, Raney nickel or Raney cobalt which may be activated with noble metals, copper chromite, palladium and platinum. The quantity of catalyst used is
25 generally 1 to 10% calculated on the quantity of polypropylene glycol which is to be reacted.

The ammonia or amine is preferably used in excess which in some cases may be considerable for example up to about 30 mols per
30 mol of polyglycol. The reaction temperatures lie between 150 and 250°C. If readily volatile compounds are used, particularly ammonia, the process is preferably carried out under
35 pressure, which may easily be as high as 300 atmospheres above atmospheric pressure.

It is generally not necessary to use solvents. If it is desired to use solvents, they should be inert, e.g. hydrocarbons, tetrahydrofuran or tertiary butyl alcohol.

40 If the ammonia or amines react sufficiently all the hydroxyl groups of the polyhydroxyl ether are converted into amino groups; these amino groups will all be primary when ammonia is used. Depending on the reaction
45 time, reaction temperature and nature and proportions of the reaction components, it is possible to obtain products which contain hydroxyl groups in the molecule in addition to the amino groups that have been formed
50 in the reaction.

The polypropylene ether amines that are obtained which contain only amino groups instead of the OH groups or which contain
55 amino groups in addition to hydroxyl groups and which may, depending on the conditions under which the reaction is carried out, be obtained as mixtures and used as such, are products that may be used for a large variety of purposes. They may be used as hardeners
60 for epoxy resins and may be converted into polyurea substances that are suitable as plasticisers or they may be cross-linked with resins which contain formaldehyde or methylol groups into substances which are used for

pressing or as bonding agents or as textile 65 finishing substances.

In order that the invention may be more fully understood, the following Examples are given, by way of illustration only:

EXAMPLE 1

1000 g. of polypropylene glycol (molecular weight 1870; OH number 62.4) obtained by
polymerisation of propylene oxide in the presence of aqueous NaOH as catalyst, 220 g.
75 liquid ammonia and 80 g. anhydrous Raney nickel were placed in an autoclave of 5 litres capacity equipped with stirring means and the pressure was raised to 20 atmospheres above
80 atmospheric pressure by addition of hydrogen and the reaction mixture was heated for 2 hours at 220°C. The pressure rose to 127 atmospheres excess pressure and dropped in the course of about 3 hours to 120 atmospheres excess pressure. The total reaction time
85 was 8 hours. The reaction product was then left to cool and depressurised at about 60°C. and the contents of the autoclave were then forced through a pressure filter. Water of reaction was then removed from the pale
90 filtrate at reduced pressure at 100°C. until the weight was constant. 922 g. of reaction product containing 95% diamine were obtained. Analytical investigation showed that
95 the residue consisted of a polyamine with secondary nitrogen. No tertiary amine nitrogen was present.

EXAMPLE 2

A mixture of 250 parts by weight polypropyleneglycol (product of addition of propylene oxide to trimethylol) propane; molecular weight 3000; OH number 59), 80 parts
100 by weight liquid ammonia and 16 parts by weight of Raney nickel were heated with stirring to 220° at an initial hydrogen pressure of 30 atmospheres excess pressure. During
105 the course of 9 hours, the pressure dropped from 166 to 160 atmospheres above atmospheric pressure. The mixture was left to cool and then filtered and the crude product was worked up as described in Example 1.
110 242 parts by weight of a faintly coloured triamine were obtained which, on analysis, was found to be 93% pure.

WHAT WE CLAIM IS:—

1. A process for the preparation of polypropylene ether amines with primary or
115 secondary amino groups which comprises reacting a polypropylene glycol of molecular weight between 1000 and 4000 and comprising at least two hydroxy groups with ammonia or
120 with a primary amine in the presence of a hydrogenation catalyst in the liquid phase at between 150° and 250°C temperatures.

2. A process as claimed in claim 1 in which the reaction with ammonia is carried
125 out under pressure.

3. A process as claimed in either claim 1

or claim 2 wherein the polypropylene glycol used as starting material is a polymersation product of propylene oxide.

- 5 4. A process as claimed in either claim 1 or claim 2 wherein the polypropylene glycol used as starting material is a reaction product of propylene oxide with a compound containing at least two reactive hydrogen atoms.

- 10 5. A process for the preparation of polypropylene ether amines substantially as herein

described with reference to either Example 1 or Example 2.

6. Polypropylene ether amines when prepared by a process as claimed in any of claims 1 to 5.

15

ELKINGTON AND FIFE,
Chartered Patent Agents,
High Holborn House,
52/54 High Holborn,
London, W.C.1.,
Agents for the Applicants.

Leamington Spa: Printed for Her Majesty's Stationery Office by the Courier Press.—1966.

Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.

BEST AVAILABLE COPY